



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08J 9/28 // A61K 47/30</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/20884</b> <b>(43) International Publication Date:</b> 12 June 1997 (12.06.97)
<b>(21) International Application Number:</b> PCT/NL96/00452 <b>(22) International Filing Date:</b> 15 November 1996 (15.11.96) <b>(30) Priority Data:</b> 9500999 6 December 1995 (06.12.95) BE <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TABAKSBLAT, Ronald [NL/NL]; Rozerye 202C, NL-6228 DP Maastricht (NL). AUSSEMS, Hendrikus, Franciscus [NL/NL]; Peutzstraat 26, NL-6412 HZ Heerlen (NL). <b>(74) Agent:</b> NIEUWKAMP, Johannes, Gerardus, Maria; Octrooiibu- reau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>
<b>(54) Title:</b> PROCESS FOR THE PREPARATION OF POROUS POLYOLEFIN PARTICLES  <div data-bbox="561 1125 1122 1520" data-label="Image"> </div> <div data-bbox="651 1562 1182 1614" data-label="Caption"> <p>SEM picture of a porous polyolefin particle, magnification 1100x</p> </div> <b>(57) Abstract</b>  <p>The invention relates to a process for the preparation of porous polyolefin particles, which process comprises the following steps: 1) dissolution of at least one crystallizable polyolefin in a solvent, which results in a solution being formed which comprises 0.1-50 wt.% polyolefin, and the initial polyolefin solution formed containing between 5 ppm and 20 wt.% of nucleating agent; 2) dispersion of the resulting polyolefin solution in a non-solvent, at a temperature that is higher than the crystallization temperature of the polyolefin in the polyolefin solution, upon which a multiphase system is formed; 3) cooling of the multiphase system, with simultaneous stirring, the cooling rate being between 0.05 and 10 °C/min, down to a temperature which is below the crystallization temperature of the polyolefin in the polyolefin solution, so that strong, polyolefin-containing particles are formed; 4) separation of the polyolefin-containing particles from the liquid(s); 5) drying of the polyolefin-containing particles at a temperature that is below the crystallization temperature of the polyolefin in the initial polyolefin solution.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

PROCESS FOR THE PREPARATION OF  
POROUS POLYOLEFIN PARTICLES

5

The invention relates to a process for the preparation of porous polyolefin particles.

A process for the preparation of porous  
10 polymer particles is known from EP-A-0370260. In this process a large number of different liquids is needed for preparation of the porous polymer particles. In the first place, a mixture of (at least) two liquids is needed to dissolve the polymer, for which a high  
15 temperature is required. A homogeneous polymer solution is then formed. Subsequently, a third liquid, a warm, inert dispersion agent, is added to the polymer solution obtained. This yields a two-phase system. This two-phase system is stirred strongly, so that drops of  
20 the polymer solution are formed. Then a fourth, cool, inert liquid is used. The drops are collected and finally an extraction step takes place. For the extraction at least a fifth liquid is required. In a number of cases extraction must be followed by washing  
25 with yet another (at least sixth) liquid, as appears from Example 11. As the known process requires the use of a large number of liquids, on an industrial scale it produces a large number of effluent streams, which need to be purified. From an environmental point of view  
30 this process is unsatisfactory, and therefore there is a need for a better process.

The aim of the invention is to provide a process for the preparation of porous polyolefin particles in which the above-mentioned drawback is  
35 eliminated or partly eliminated. This aim is achieved in that the process comprises the following steps:

- 2 -

- 1) dissolution of at least one crystallizable polyolefin in a solvent, which results in a solution being formed which comprises 0.1-50 wt.% polyolefin, and the initial polyolefin solution  
5 formed containing between 5 ppm and 20 wt.% of nucleating agent,
- 2) dispersion of the resulting polyolefin solution in a non-solvent, at a temperature that is higher than the crystallization temperature of the  
10 polyolefin in the polyolefin solution, upon which a multiphase system is formed,
- 3) cooling of the multiphase system, with simultaneous stirring, the cooling rate being between 0.05 and 10°C/min, down to a temperature  
15 which is below the crystallization temperature of the polyolefin in the polyolefin solution, so that strong, polyolefin-containing particles are formed,
- 4) separation of the polyolefin-containing particles  
20 from the liquid(s),
- 5) drying of the polyolefin-containing particles at a temperature that is below the crystallization temperature of the polyolefin in the initial polyolefin solution.

25

Thus it is achieved that in the process according to the invention fewer (different) liquids are needed on an industrial scale, which has as a direct consequence that fewer effluent streams need to  
30 be purified and the process can be carried out more simply than the process as described in EP-A-02370260. In addition, in the process according to the invention the risk of the porous polyolefin prepared carrying the odour of one or more of the liquids is smaller.

35 Moreover, the process of the present invention appears to have an advantage in that the dimensions of the porous polyolefin particles and the pore size are

- 3 -

better controllable. Another advantage is that the dimensions of the porous polyolefin particles prepared exhibit a less high spread than in the state of the art.

5           It is true that EP-A-0644230 discloses a process for the preparation of polymer particles with controllable dimensions, but it does not give any clue as to how porous polymer particles should be prepared.

10           The porous polyolefin particles obtained by use of the process according to the invention can be prepared using a wide variety of polyolefins. Not only homopolymers are suitable, use can also be made of copolymers. The term copolymers is understood to mean those polymers which contain two or more different  
15           monomers. Within the scope of the invention it is also possible to use mixtures of different polyolefins.

          For the polyolefins use can be made of, for example, entirely freshly made polyolefins, polyolefins obtained after reprocessing of used materials, for  
20           example in the framework of recycling, polyolefins collected as production rejects and production waste, contaminated polyolefins and polyolefins that do not satisfy the predetermined product requirements, the so-called off-spec products.

25           Suitable polyolefins for use in the process according to the invention are, for example, polyethylene, polypropylene, polybutene, poly(4-methyl-1-pentene), polycyclohexylethylene. Preferably, use is made of polyethylene and/or polypropylene, more  
30           preferably use is made of polyethylene. It is not critical which type of polyethylene is used in the process according to the invention. The polyethylene may for example have been prepared using processes known per se, including solution, slurry, gas-phase and  
35           high-pressure processes. Use can be made for example of ultrahigh-molecular-weight polyethylene (UHMWPE), high-density polyethylene (HDPE), linear low-density

polyethylene (LLDPE), low-density polyethylene (LDPE), very-low-density polyethylene (VLDPE) and ultralow-density polyethylene (ULDPE). Preferably, use is made of LDPE or LLDPE.

5 LLDPE is understood to mean a substantially linear homo- or copolymer of ethylene with one or more  $\alpha$ -olefins with 3-12 C atoms and optionally one or more non-conjugated dienes, the product having a density of 910-965 kg/m<sup>3</sup>. Examples of suitable  $\alpha$ -olefins are  $\alpha$ -  
10 alkenes with 3-9 C atoms, in particular propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. Examples of suitable dienes are 1,7-octadiene and 1,9-decadiene. LLDPE mainly has short side chains of 1 to 10 C atoms and substantially fewer long side chains  
15 than LDPE.

As LDPE use can for example be made of polyethylene produced in the customary manner in a high-pressure process using one or more radical initiators. The density of LDPE is lower than 935  
20 kg/m<sup>3</sup>.

If polypropylene is used, use may be made of both isotactic and syndiotactic polypropylene.

In the process according to the invention the following takes place. The polyolefin is first  
25 dissolved in a solvent. Various organic liquids may be used as solvent. The choice of the solvent will to a large extent be determined by the degree to which the solvent is capable of dissolving the polyolefin. Examples of suitable organic solvents for use in the  
30 process of the present invention are compounds from the series of n-alkanes, i-alkanes, cycloalkanes, polycyclic compounds with two or more cyclic structures, alkenes, cycloalkenes, optionally hydrogenated and/or substituted aromatics, chlorinated  
35 hydrocarbons, esters, aldehydes, alcohols, ketones, ethers, decalin, tetralin, paraffin oil or xylenes. Mixtures of these are also suitable. If polyethylene is

used as polyolefin, use is preferably made of a cycloalkane or n-alkane, in particular cyclohexane, n-hexane or n-heptane.

Dissolution of the polyolefin in the solvent optionally takes place with simultaneous heating. If necessary dissolution can be accelerated by applying dynamic or static mixing. Depending on the choice of solvent, it may be advantageous to work at elevated pressure. Dissolution of the polyolefin yields a polyolefin solution.

So much polyolefin is used that the polyolefin solution formed contains between 0.1 and 50 wt.%, preferably between 1 and 30 wt.%, polyolefin. This weight percentage is calculated on the basis of the sum of the weight of the solvent and that of the polyolefin. At concentrations >50 wt.% it becomes difficult to stir the polyolefin solution; at low concentrations the process becomes less interesting from an economic point of view.

To obtain porous polyolefin particles it is necessary for the polyolefin to be crystallizable. However, it is not necessary for the polyolefin to be fully (100%) crystallizable.

Further it is necessary for between 5 ppm and 20 wt.%, preferably between 10 ppm and 10 wt.%, nucleating agent to be present in the polyolefin solution, the weight percentage being calculated on the basis of the sum of the weight of the polyolefin and that of the nucleating agent. A high concentration of nucleating agent leads to small particles, while at a low concentration of nucleating agent large particles are formed. Moreover, at a too low concentration the crystallization process is too slow to be of industrial interest. The moment of addition of the nucleating agent is not critical, provided the nucleating agent is present before the multiphase system is cooled. Preferably, the nucleating agent is added when the

polyolefin solution is being prepared. The addition mode is not critical, either. The nucleating agent can be added at once, continuously, or in several portions over a certain period of time.

5            Preferably, the nucleating agent is selected from the series formed by silicates, mica, talc, sorbitol derivatives, saturated or unsaturated fatty acids or their salts, organic pigments or polymers with functional groups. It is also possible to add a  
10 combination of these compounds. More preferably, the nucleating agent is selected from talc, a sorbitol derivative or an oxidized polymer.

          The fatty acids and their salts which are used as nucleating agent may contain 10 to 100 C atoms;  
15 examples are lauric acid, stearic acid and the mixture of alkane carboxylic acids that is known as 'Montanwachs'. The salts of the fatty acids may contain a metal ion from groups 1, 2, 11, 12, 13 and 14 of the  
20 Periodic System of the Elements, as published in the CRC Handbook of Chemistry and Physics, 70th Edition, 1989-1990. Preferably, sodium stearate, potassium stearate, calcium stearate, magnesium stearate or zinc stearate is chosen.

          Polymers with functional groups based on  
25 polyolefins may for example be obtained through grafting, copolymerization or oxidation of polyolefins or by subjecting polyolefins to a surface treatment. These polymers usually have between 0.1 and 15 wt.% functional groups.

30            If the crystallizable polyolefin already contains enough functional groups for example as a consequence of previous treatments, it is not necessary to add an additional nucleating agent.

          The resulting polyolefin solution with  
35 nucleating agent and a non-solvent are dispersed in each other, optionally with stirring or another form of dynamic or static mixing. The order in which non-



solvent and polyolefin solution are added to each other to be dispersed is not critical, as long as the non-solvent remains the continuous phase in the dispersion obtained. The non-solvent is a compound in which the polyolefin does not dissolve and which is also immiscible with the polyolefin solution. For suitable solvents and non-solvents, the reader is referred to the tables as presented in Polymer Handbook, J. Brandrup and E.H. Immergut, eds., John Wiley and Sons, 3rd Ed. (1989), p. VII/379 ff. The amount of non-solvent to be used is not critical as long as the non-solvent remains the continuous phase in the dispersion obtained.

Depending on the polarity of the polyolefin, the non-solvent is a polar or apolar compound.

For a polyolefin that dissolves in an apolar solvent, a polar non-solvent will be very suitable. Suitable polar compounds for use as non-solvent are, for example, water or a compound from the group of organic or inorganic acids, ketones or alcohols. Preferably, water, acetone, methanol or ethanol are used, and more preferably use is made of water. Mixtures of these compounds are also suitable. Examples of apolar compounds that are suitable for use as non-solvent are aliphatic, alicyclic, aromatic and polycyclic hydrocarbons. Mixtures of these compounds are also suitable. The compounds may be either substituted or unsubstituted. The substituent group may consist either of only C and H atoms or of C, H and/or heteroatoms. The substituent group preferably has 3-100 C atoms.

During dispersion of the polyolefin solution in the non-solvent a multiphase system is formed, the term multiphase system being understood to mean a system comprising at least two phases, of which at least one phase contains polyolefin: the polyolefin-containing phase. During dispersion of polyolefin

solution and non-solvent the temperature must be higher than the crystallization temperature of the polyolefin in the polyolefin solution.

The crystallization temperature can be  
5 determined by means of the Differential Scanning  
Calorimetry technique. During a Differential Scanning  
Calorimetry (DSC) measurement the substance is  
subjected to controlled heating or cooling in a  
controlled atmosphere, while the difference in  
10 temperature between the substance and a reference  
material due to energy changes in the substance is  
measured continuously. A transition (such as melting or  
crystallization) is marked by absorption or release of  
energy by the substance, resulting in a corresponding  
15 endothermal or exothermal peak in the DSC curve. It is  
possible for more than one peak to be present in the  
curve. Determination of the crystallization temperature  
of a polymer in a solvent can best be carried out by  
using the same solvent also during the DSC measurement.  
20 Depending on the choice of the solvent, use will be  
made of open or pressure-tight specimen holders. If  
cyclohexane is used as solvent, for example, pressure-  
tight specimen holders will be chosen in view of the  
high vapour pressure. A controlled atmosphere is  
25 obtained, for example, by the use of nitrogen or  
helium.

The position of the melting point or  
crystallization point can be affected by a number of  
factors, including the particle size, the heating or  
30 cooling rate or the inhomogeneity of the specimen. In  
the DSC measurements carried out within the scope of  
the invention use is made of a heating or cooling rate  
of 5°C/min.

As crystallization temperature the  
35 temperature is used that belongs to the point where the  
(DSC) crystallization curve deflects 1% from the base  
line, the percentage relating to the height of the

maximum peak.

To control the dimensions of the drops of the polyolefin solution, which together make up the polyolefin-containing phase, it may be useful to add a surfactant to the non-solvent. The surfactant concentration is preferably 10 ppm - 5 wt.%, more preferably 100 ppm - 1 wt.%. The weight percentage is calculated on the basis of the sum of the weight of the non-solvent and the surfactant together. At too low a surfactant concentration the drops of the polyolefin solution may exhibit too much affinity to aggregation. However, if the surfactant concentration is too high, too many small drops of polyolefin solution may be formed, which after drying form too small particles. For the average person skilled in the art it is easy to determine the most desirable concentration by means of experiments.

The surfactant may be an anionic, cationic, non-ionic or amphoteric surfactant. Suitable surfactants are, for example, compounds from the group of alkane sulphonates, alkyl benzene sulphonates, fatty alcohol sulphonates, alkyl ammonium compounds, surfactants of the betaine type and fatty alcohol polyglycol ethers. If polyethylene is used as polyolefin, use is preferably made of an alkane sulphonate or a fatty alcohol polyglycol ether.

On account of the presence of one or more surfactants, foaming may occur. To prevent foaming, a foam inhibitor and/or a defoaming agent can be added. A combination of foam inhibiting and/or defoaming agents is also possible. These foam inhibitors and/or defoaming agents can be added in various steps of the process, but this is preferably done during dispersion.

Optionally, a portion of the solvent can be evaporated from the multiphase system formed in the process according to the invention. Whether or not evaporation is necessary will depend on the polyolefin

and the solvent started from and the initial polyolefin concentration. The objective of evaporation is concentration of the polyolefin solution to such an extent that during cooling polyolefin-containing particles, also referred to as gel particles, are formed which can be processed according to the process of the present invention. The amount of solvent to be evaporated depends on the concentration of the polyolefin solution. The lower the concentration, the larger the amount that can be evaporated. Polyolefin-containing particles or gel particles are here understood to mean the particles that are separated from the multiphase system and that still contain solvent and optionally non-solvent. The need for evaporation and the degree to which such evaporation should take place can readily be established experimentally by one skilled in the art. Solvent evaporation can lead to simultaneous evaporation of a portion of the non-solvent. In a large number of cases evaporation of an azeotrope will be possible. In special cases the non-solvent may, because of the choice of the solvent and the non-solvent, have a tendency to be evaporated at lower temperatures than the solvent. If this situation arises, any deficiency in terms of the non-solvent is to be made up using fresh or recycled non-solvent. The result aimed for, an increased concentration of the polyolefin in the solvent, will then also be achieved in this manner.

The remaining multiphase system is then cooled in a controlled manner. Cooling usually takes place at a rate that is between 0.05 and 10°C/min, but preferably at a rate that is between 0.1 and 5°C/min, and in particular between 0.2 and 2°C/min. During cooling, due to crystallization, polyolefin-containing particles are formed in the multiphase system that still contain solvent and optionally non-solvent. Cooling is continued until the multiphase system has

- 11 -

reached a temperature that is below the crystallization temperature of the polyolefin in the polyolefin solution. For further processing the polyolefin-containing particles must be strong enough to be  
5 subjected to separation and drying operations. If the temperature is still too high, the polyolefin-containing particles are too weak for proper filtration. If this is the case, deeper cooling is to be applied. If cyclohexane and/or n-heptane is used as  
10 solvent for polyethylene, cooling preferably takes place until the temperature is below 40°C. As already described, the crystallization temperature can be determined by means of the DSC technique.

During cooling stirring must be applied.  
15 Within the scope of the invention stirring is understood to mean maintaining the dispersion. When other means are able to achieve and maintain the dispersion, these means are also suitable. The particle size can be controlled depending on the type of stirrer  
20 and the speed. The higher the stirring speed (with the same type of stirrer), the smaller the porous polyolefin particles will be, and the lower the stirring speed, the larger the particles will be.

Subsequently, the polyolefin-containing  
25 particles are separated from the multiphase system. This can be done in a way known to the average person skilled in the art. Examples of suitable techniques are vacuum filtration, centrifuging and/or treatment in a filtration press; preferably, gravity-based filtration  
30 is used.

In the last step, the separated polyolefin-containing particles, still containing solvent and optionally non-solvent, are dried. Drying can be effected up to any desired degree of solvent removal.  
35 The way the drying process is effected to a major extent determines the porosity of the polyolefin particles. The drying process needed to obtain porous

- 12 -

polyolefin particles can be carried out in various ways; thus, for example, drying can be effected at reduced pressure, the polyolefin-containing particles can be stripped using a gas or vapour, or the

5 polyolefin-containing particles can be dried dielectrically (for example by means of microwave or RF (radio frequency) drying, as described for example in Microwave Processing and Engineering, R.V. Decareau and R.A. Peterson, ed. Ellis Horwood Ltd and VCH GmbH,

10 1986, or in Industrial Microwave Heating, A.C. Metaxas and R.J. Meredith, Peter Peregrinus Ltd., 1983). In these options the solvent has a reduced partial pressure.

Examples of gases that are suitable for use

15 in the stripping process are air, nitrogen, helium, carbon dioxide and methane. Preferably, nitrogen is used as stripping gas.

Drying at reduced pressure preferably takes place under such conditions that the partial pressure

20 of the solvent in the vapour phase is less than 50%, but more preferably less than 20%, of the standard vapour pressure of the solvent at 20°C.

The temperature during drying must be lower than the crystallization temperature of the polyolefin

25 in the polyolefin solution. If use is made of polyethylene as polyolefin, for example, drying preferably takes place at a temperature below 30°C.

Irrespective of the type of drying process that is chosen, drying preferably takes place under

30 such conditions that degradation of the particle structure is prevented as much as possible (for example by low force effects). Any degradation of the particle structure can simply be established in one or more experiments by one skilled in the art.

35 Use of the process of the present invention makes it possible to obtain porous polyolefin particles with dimensions between 0.1 and 20 mm. By way of

illustration some electron microscopy (SEM) pictures of porous polyolefin particles, obtained by use of the process according to the invention, are shown in Figures 1 up to and including 6.

5           The porous polyolefin particles prepared using the process according to the invention are suitable for various applications, for example as concentrates, absorbents or carriers for substances that are to be released at a slow and/or controlled  
10 rate.

For proper dispersion of additives in a plastic is it advantageous, and sometimes necessary, to add the additives to the plastic in the form of a concentrate of the additive in a polymeric matrix.  
15 Concentrates, for example, are widely used in plastics as so-called masterbatches. For economic use of the additives it is advantageous for the additive concentration in the polymeric matrix of the masterbatch to be as high as possible. However,  
20 particularly in the case of liquid additives, it often proves impossible to effect proper dispersion of high concentrations of the additive in the polymeric matrix. Porous polyolefin particles obtained by use of the process according to the invention are eminently  
25 suitable for absorption of high concentrations of additive. If liquid additives are used, the additive can be absorbed directly. If the additive is in solid form, the additive can be melted, dissolved or dispersed in a suitable liquid before being contacted  
30 with the porous polyolefin particle. Absorption of the additive in the porous polyolefin particle can be carried out using known techniques, one suitable technique being dosing of the additive to the porous polyolefin particle in a mixer.

35           In another application of these porous polyolefin particles the particles can be used to effect the slow release of an active substance. To this

- 14 -

end the active substance is first absorbed by the porous polyolefin particle, upon which the substance in question is slowly released. As examples of active substances, drugs, fragrances, insecticides, pheromones and fertilizers may be mentioned.

Furthermore, porous polyolefin particles are suitable for (selective) absorption of certain substances. Examples are the absorption of stench components, leaked and/or spilled liquids or purification of contaminated water streams, with the porous polyolefin particle absorbing the contaminants.

The invention will be explained on the basis of the following examples, without being limited thereto.

In the examples the density,  $d$ , is understood to mean the density as determined according to ASTM standard D792-66. The melt index, M.I., is determined according to ASTM standard D1238, condition E.

The DSC measurements were performed on a Perkin-Elmer DSC 7. The temperature and energy calibrations were performed on the basis of the melting of indium and lead. The temperature measurement during cooling is checked on the basis of the solid-solid transition of 4,4'-azoxy-anisole. During the measurement a heating and cooling rate of 5°C/min was used.

The porosity is determined by means of Hg porosimetry on an Autopore II 9220 supplied by Micromeritics (USA).

#### Example I

In an Erlenmeyer flask 45 g of LDPE having a density of 918 kg/m<sup>3</sup> and an M.I. of 8 dg/min was dissolved in 330 g of cyclohexane at about 80°C under reflux of the cyclohexane. 0.38 g of di-(ethyl benzyldiene) sorbitol (the product NC-4 supplied by Mitsui Toatsu) was added to the solution as nucleating



- 15 -

agent. The solution was dosed to a beaker containing 750 g of water of about 65°C, to which 0.63 g of a surfactant (an alkane sulphonate having an average chain length of 14.5 C atoms) has been added. While the mixture was being stirred, with a power input of about 200 W/m<sup>3</sup>, it was dispersed for 20 minutes, upon which a portion of the cyclohexane evaporated. Subsequently, the mixture was cooled to room temperature with an average cooling rate of about 0.6 °C/min. The mixture was screened, so that strong, predominantly round gel particles with a particle size of about 2-3 mm were obtained. These particles were dried in a vacuum stove at room temperature and a pressure of <100 mbar (<10<sup>4</sup> N/m<sup>2</sup>). Porous polyethylene particles were formed. The porosity of the particles was 0.99 cm<sup>3</sup>/g; 80% of the pores in the porous polyolefin particles had a pore radius between 0.6 and 2.2 μm.

#### Example II

In an Erlenmeyer flask 54 g of LDPE having a density of 918 kg/m<sup>3</sup> and an M.I. of 8 dg/min was dissolved in 330 g of cyclohexane at about 80°C under reflux of the cyclohexane. 0.016 g of talc (the product M-03 supplied by Finntalc) was added to the solution as nucleating agent. This mixture was dosed to a beaker containing 750 g of water of about 65°C, to which 0.57 g of a surface-active agent (an alkane sulphonate having an average chain length of 14.5 C atoms) has been added. While the mixture was being stirred, with a power input of about 200 W/m<sup>3</sup>, it was dispersed for 15 minutes, upon which a portion of the cyclohexane evaporated. Subsequently, the mixture was cooled to room temperature with an average cooling rate of about 0.5 °C/min. The mixture was screened, so that strong, predominantly round gel particles with a particle size of about 1-2 mm were obtained. These particles were dried in a vacuum stove at room temperature and a

- 16 -

pressure of <100 mbar (<10<sup>4</sup> N/m<sup>2</sup>). Porous polyethylene particles were formed. The porosity of the particles was 1.87 cm<sup>3</sup>/g; 80% of the pores in the porous polyolefin particles had a pore radius between 0.6 and 2.2 μm.

#### Comparative experiment A

In an Erlenmeyer flask 45 g of LDPE having a density of 918 kg/m<sup>3</sup> and an M.I. of 8 dg/min was dissolved in 330 g of cyclohexane at about 80°C under reflux of the cyclohexane. This solution was dosed to a beaker containing 750 g of water of about 65°C, to which 1.5 g of a surfactant (an alkane sulphonate having an average chain length of 14.5 C atoms) has been added. No nucleating agent was present. While the mixture was being stirred, with a power input of about 200 W/m<sup>3</sup>, it was dispersed for 15 minutes, upon which a portion of the cyclohexane evaporated. Subsequently, the mixture was cooled to room temperature with an average cooling rate of about 0.8 °C/min. The mixture was screened, upon which a slurry of LDPE and cyclohexane was formed, in which no well-defined particles could be distinguished. Upon drying to the outside air a hard cake was formed.

#### Example III

10 wt.% of a liquid additive (alkylamine ethoxylate, the product Atmer 163 supplied by ICI) was added to the product of Example I with gentle shaking. The additive was fully taken up within a few minutes, upon which granules were obtained that feel dry to the touch. Then, in 10% increments, more additive was added to this product. The maximum load upon which the product obtained still feels dry to the touch was 60 wt.%.

Example IV

The gel particles obtained according to the process in Example I were now dried at a pressure of <100 mbar ( $<10^4$  N/m<sup>2</sup>) and a temperature setting of the stove of 35°C. To the product now obtained 5 wt.% of a liquid additive (alkylamine ethoxylate, the product Atmer 163 supplied by ICI) was added with gentle shaking. The additive was fully taken up within a few minutes, upon which granules were obtained that feel dry to the touch. Then, in increments of 5 wt.%, more additive was added to this product. The maximum load at which a product was obtained that still feels dry to the touch was 25 wt.%. This proves that the maximum load of particles dried at 35% is much lower than the maximum load of particles dried at room temperature.

Example V

The gel particles of example I were now dried at a pressure of <100 mbar ( $<10^4$  N/m<sup>2</sup>) and a temperature setting of the stove of 50°C. To the product now obtained 5 wt.% of a liquid additive (alkylamine ethoxylate, the product Atmer 163 supplied by ICI) was added with gentle shaking. The additive was fully taken up within a few minutes, upon which granules were obtained that feel dry to the touch. Then, in increments of 5 wt.%, more additive was added to this product. The maximum load upon which a product is obtained that still feels dry to the touch was 10 wt.%. The examples prove that the higher the temperature at which the particles are dried, the lower the maximum load can be.

C L A I M S

1. Process for the preparation of porous polyolefin particles, which process comprises the following steps:
  - 1) dissolution of at least one crystallizable polyolefin in a solvent, which results in a solution being formed which comprises 0.1-50 wt.% polyolefin, and the initial polyolefin solution formed containing between 5 ppm and 20 wt.% of nucleating agent,
  - 2) dispersion of the resulting polyolefin solution in a non-solvent, at a temperature that is higher than the crystallization temperature of the polyolefin in the polyolefin solution, upon which a multiphase system is formed,
  - 3) cooling of the multiphase system, with simultaneous stirring, the cooling rate being between 0.05 and 10°C/min, down to a temperature which is below the crystallization temperature of the polyolefin in the polyolefin solution, so that strong, polyolefin-containing particles are formed,
  - 4) separation of the polyolefin-containing particles from the liquid(s),
  - 5) drying of the polyolefin-containing particles at a temperature that is below the crystallization temperature of the polyolefin in the initial polyolefin solution.
2. Process according to claim 1, characterized in that, before the multiphase system is cooled, a portion of the solvent is evaporated from the multiphase system formed.
3. Process according to either one of claim 1 or 2, characterized in that the polyolefin is a polyethylene.

4. Process according to claim 3, characterized in that the solvent is cyclohexane, n-hexane or n-heptane.
5. Process according to any one of claims 1-4, characterized in that the polyolefin concentration in the polyolefin solution is between 1 and 30 wt.%.  
5
6. Process according to any one of claims 1-5, characterized in that the nucleating agent is chosen from the following compounds: silicates, mica, talc, sorbitol derivatives, saturated or unsaturated fatty acids or their salts, organic pigments, polymers with functional groups, or a combination of these.  
10
7. Process according to claim 6, in which the nucleating agent is talc, a sorbitol derivative or an oxidized polymer.  
15
8. Process according to any one of claims 1-7, characterized in that the polar compound is water, acetone, methanol, ethanol or a mixture of these compounds.  
20
9. Process according to any one of claims 1-8, characterized in that the non-solvent contains a surface-active agent.
- 25 10. Process according to any one of claims 1-9, characterized in that the multiphase system is subjected to cooling at a rate that is between 0.1 and 5°C/min.
- 30 11. Process according to claim 10, characterized in that the multiphase system is subjected to cooling at a rate that is between 0.2 and 2°C/min.
12. Process according to any one of claims 1-11, characterized in that, upon drying under reduced pressure, the partial pressure of the solvent in the vapour phase is less than 20% of the standard vapour pressure of the solvent at 20°C.  
35
13. Use of the porous polyolefin particles obtained

according to the process of any one of claims 1-12  
as concentrate, absorbent or carrier for  
substances that are to be released slowly or in a  
controlled manner.

1/3

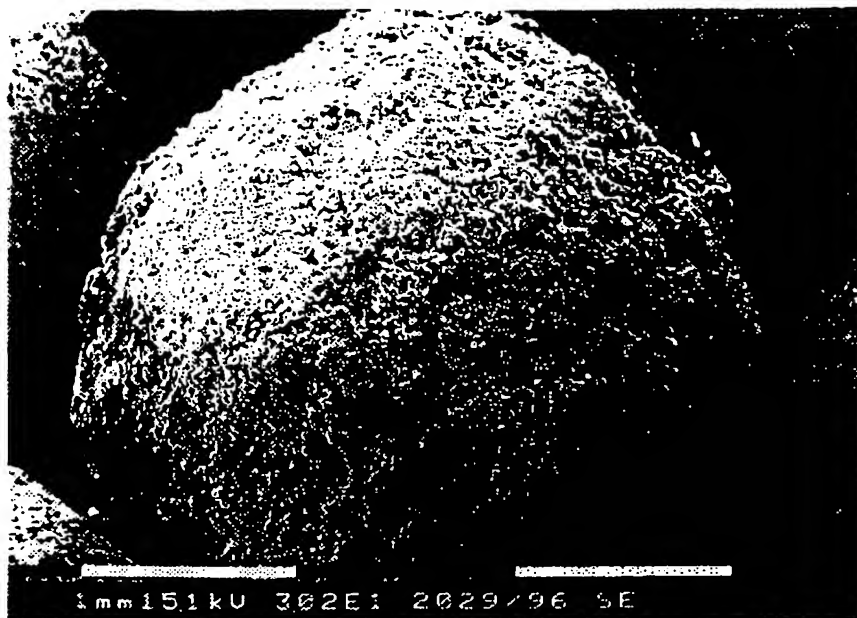


Figure 1 SEM picture of a porous polyolefin particle,  
magnification 30x



Figure 2 SEM picture of a porous polyolefin particle,  
magnification 120x

**BEST AVAILABLE COPY**  
**SUBSTITUTE SHEET (RULE 26)**

2/3

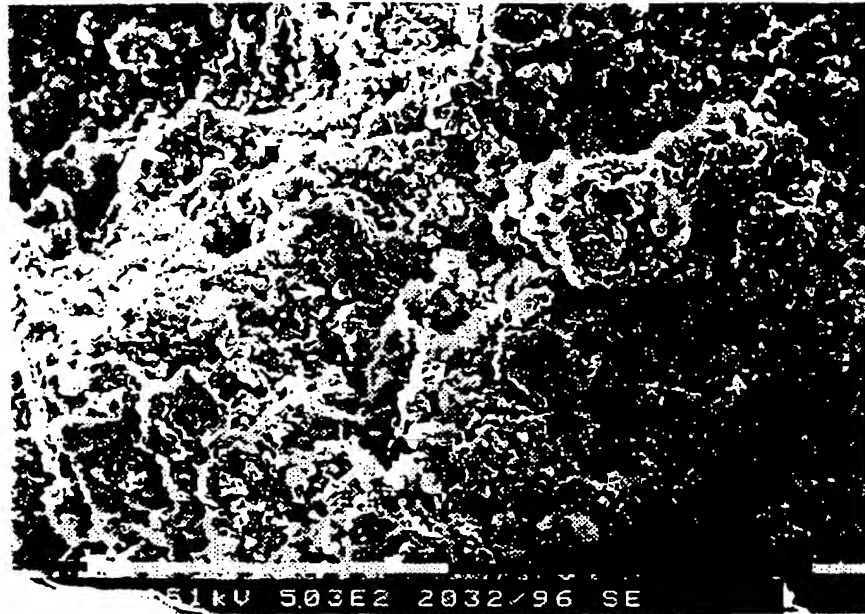


Figure 3 SEM picture of a porous polyolefin particle, magnification 500x

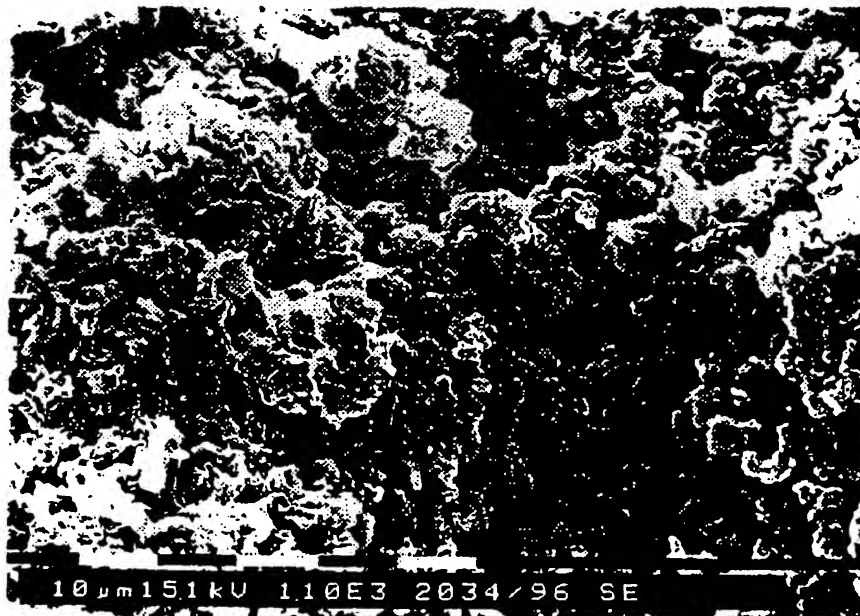


Figure 4 SEM picture of a porous polyolefin particle, magnification 1100x

BEST AVAILABLE COPY  
SUBSTITUTE SHEET (RULE 26)



3/3



Figure 5 SEM picture of a porous polyolefin particle, magnification 1100x

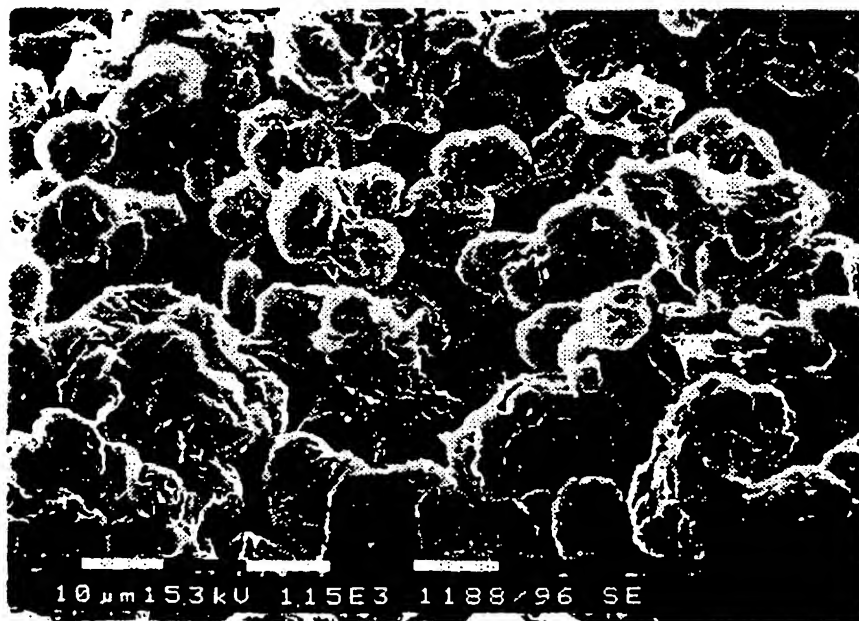


Figure 6 SEM picture of a porous polyolefin particle, magnification 1150x

# INTERNATIONAL SEARCH REPORT

International Application No

PC1/NL 96/00452

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08J9/28 //A61K47/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 226 320 A (ICI PLC) 27 June 1990 see page 7, line 24 - page 8, line 4 see claims ---	1,3,5, 10-12
A	EP 0 222 718 A (NILSSON KJELL G C ; MOSBACH KLAUS H (SE)) 20 May 1987 ---	1-13
A	US 4 673 695 A (AUBERT JAMES H ET AL) 16 June 1987 see column 7, line 3-37 see claims 1,2 ---	1,2,5,6
A	EP 0 273 582 A (MINNESOTA MINING & MFG) 6 July 1988 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

12 February 1997

Date of mailing of the international search report

21.02.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Oudot, R

# INTERNATIONAL SEARCH REPORT

International Application No

PC1/NL 96/00452

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 3 308 073 A (KEPPLE, JAMES E.) 7 March 1967  see claims</p> <p>-----</p>	1

# INTERNATIONAL SEARCH REPORT

Inter nal Application No  
PCT/NL 96/00452

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2226320	27-06-90	NONE	
EP-A-0222718	20-05-87	SE-B- 464816 DE-D- 3689327 DE-T- 3689327 JP-B- 8030124 JP-A- 62169837 SE-A- 8504764 US-A- 5015576 US-A- 4935365	17-06-91 05-01-94 16-06-94 27-03-96 27-07-87 16-04-87 14-05-91 19-06-90
US-A-4673695	16-06-87	NONE	
EP-A-0273582	06-07-88	US-A- 4726989 AU-B- 590129 AU-A- 8058487 CA-A- 1318472 DE-A- 3785655 DE-T- 3785655 HK-A- 40194 JP-A- 63161035 KR-B- 9511717 SG-A- 42994	23-02-88 26-10-89 16-06-88 01-06-93 03-06-93 14-10-93 06-05-94 04-07-88 09-10-95 25-11-94
US-A-3308073	07-03-67	NONE	